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Mercury and Arsenic Bioaccumulation and Eutrophication in Baiyangdian Lake, China

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Abstract

Hg and As are widespread contaminants globally and particularly in Asia. We conducted a field study in Baiyangdian Lake, the largest lake in the North China Plain, to investigate bioaccumulation and trophic transfer of potentially toxic metals (total mercury and arsenic) in sites differing in proximity from the major point sources of nutrients and metals. Hg concentrations in fish and As concentrations in water are above critical threshold levels (US Environmental Protection Agency based) considered to pose some risk to humans and wildlife. Hg concentrations in biota are within the range of concentrations in lakes in the Northeast US despite the high levels of Hg emission and deposition in China whereas As concentrations are much higher. Dissolved concentrations of both Hg and As decrease with increasing chlorophyll concentrations suggesting that there is significant uptake of metal from water by algae. These results provide evidence for algal blooms controlling dissolved metal concentrations and potentially mitigating the trophic transfer of Hg to fish. This study also underscores the need for further investigation into this contaminated ecosystem and others like it in China that are an important source of fish and drinking water for consumption by local human populations.

Keywords

Mercury; arsenic; bioaccumulation; lake; eutrophication; China

Introduction

Metal pollution and eutrophication are common problems in freshwater ecosystems throughout the industrialized world [Nriagu, 1996; Carpenter *et al.*, 1998]. Inputs of sewage and industrial contaminants into waterways in China are increasing with rapid economic

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development [Liu and Diamond, 2005]. There are major atmospheric emissions of Hg and As due to coal combustion and resulting Hg deposition to land and water surfaces particularly surrounding urban and industrial areas [Finkelman et al., 1999; Xia and Liu, 2004; Pacyna et al., 2006; Wu et al., 2006]. China is the world's largest producer and consumer of coal [Jiang et al., 2006]. Global emissions of Hg are a major problem in Asia with the region contributing 54% from anthropogenic sources and China alone contributing the most (600 tons of Hg comprising 28% of the global total) [Pacyna et al., 2006]. These emissions result in both regional and local deposition [Wang et al., 2006]. In addition, metals such as Cd, Pb, and Cr, and nutrients are discharged into surface waters from a variety of industrial and municipal facilities [Cheng, 2003] and As contamination of waterways from both geologic and anthropogenic sources is widespread [Smedley and Kinniburgh, 2002; Zhang et al., 2002].

China derives a major portion of its fisheries production from freshwater culture in ponds, reservoirs, lakes, and river channels [Zhong and Power, 1997; Liu and Diamond, 2005]. In most cases, these water bodies are extremely eutrophic receiving nutrients from both agricultural runoff, human waste, and the aquaculture itself. Many water bodies also receive direct discharges of metal contaminants in addition to atmospherically deposited metals [Zhang et al., 1999; Wang and Stuanes, 2003]. Metals accumulate in biota and their mode of uptake is highly dependent on the metal. Bioaccumulation in fish and shellfish represent an exposure route for these atmospheric contaminants such as Hg to humans [Munthe et al., 2007]. Moreover, reservoir formation for agriculture or hydroelectric power can produce a significant increase in mercury concentrations in fish inhabiting the reservoirs [Bodaly et al., 1984; Jackson, 1991; Jin et al., 1999; Kidd et al., 1999]. In China, fish consumption is known to be the most important exposure route for Hg and yet very little research has been conducted on Hg trophic transfer in aquatic food webs and virtually none on freshwater food webs [Jiang et al., 2006; Li et al., 2006].

Bioaccumulation of metal contaminants in aquatic food webs vary by metal and with ecological factors such as trophic level, the feeding strategy of an organism, and organism abundance within a trophic level. Higher trophic levels are correlated with higher concentrations of Hg due to biomagnification but lower concentrations of As due to biodiminution [Cabana et al., 1994; Chen and Folt, 2000; Chen et al., 2000; Burgess and Hobson, 2006]. Moreover, fish that consume benthic prey appear to bioaccumulate lower Hg burdens than those predominantly consuming pelagic prey [Watras et al., 1998; Power et al., 2002; Essington and Houser, 2003; Gorski et al., 2003]. Metal bioaccumulation within a trophic level is also related to nutrient status, algal densities, and growth rates [Pickhardt et al., 2002; Karimi et al., 2007].

The most widespread and studied human impact on lake ecosystems is nutrient enrichment and subsequent eutrophication. In China, uncontrolled nutrient inputs to waterbodies and their proximity to agriculture and use in aquaculture has resulted in severe eutrophication in most of the country's lakes due to these human impacts. However, nutrient enrichment in lakes which increases algal blooms may decrease the concentrations of dissolved metals in the water due to uptake by the algae [Luoma et al., 1998; Pickhardt et al., 2002; Chen and Folt, 2005]. It can also dilute the metals transferred to higher trophic levels via the processes

of bloom and density dilution in which the increase in algal biomass reduces the mass specific concentrations of metal in algae and slows the rate of trophic transfer to zooplankton [Pickhardt *et al.*, 2002; Chen and Folt, 2005]. In addition, higher phosphorus content of food could result in enhanced growth of individual consumers and resulting growth dilution of contaminant [Karimi *et al.*, 2007]. Hence the potential interaction of nutrient and metal contaminants in Chinese lakes could have important influences on the actual bioaccumulation and trophic transfer of metals in aquatic food webs.

Here we report on a study conducted in Baiyangdian Lake, the largest freshwater body in the North China Plain that receives nutrient inputs from sewage discharge and aquaculture, and industrial contaminants from factories in the nearby city of Baoding. The lake consists of more than 100 small and shallow lakes linked by thousands of ditches with a surface area of 366 km² (when full), a catchment of 31,200 km², average depth of 9 m, and latitude and longitude coordinates of 38°44'-49' and 115°45'-116°07', respectively [Xu *et al.*, 1998]. In recent decades, the persistent water withdrawals for irrigation and periods of severe drought have resulted in a major decline in water level and lake area as well as fish kills associated with anoxic events.

Extensive studies of Baiyangdian over the last 50 years by the Chinese Academy of Sciences, document increased inputs of contaminants, particularly sewage. Sewage treatment plants discharge not only nutrients, but also metal contaminants not removed by the treatment process [Wang *et al.*, 2003]. Previous studies of the lake show organic contaminants such as DDT (dichloro-diphenyl-trichloroethane) and lindane are bioaccumulated and biomagnified in the food chain (Dou *et al.*, 1998). At the same time, fisheries yields and benthic and planktonic diversity have decreased [Xu *et al.*, 1995; Xu *et al.*, 1998]. The distance of sites to sewage outfalls of the nearby Baoding City relate positively to the biodiversity of invertebrate organisms [Xu *et al.*, 1998]. Most of the research in Baiyangdian has investigated bioaccumulation of organic contaminants and effects of eutrophication on community diversity. However, bioaccumulation of metal contaminants in the food web or its relationship to nutrient enrichment has not been studied in this highly impacted lake.

The main objective of this study was to investigate metal bioaccumulation in aquatic organisms at different trophic levels in Baiyangdian Lake as it relates to eutrophication and proximity to pollution sources. Here, we examined Hg and As, a metal and a metalloid, both elements with important human health effects but contrasting chemical characteristics and fate in aquatic food webs. We also compared metal bioaccumulation from this polluted system to those of relatively uncontaminated lake food webs in the Northeastern U.S. where the patterns of metal fate are fairly well understood [Chen and Folt, 2000; Chen *et al.*, 2000]. In this study, we chose to address three questions: 1) Are metal concentrations in water related to nutrient, chlorophyll *a*, and zooplankton densities? 2) Do Hg and As biomagnify or biodiminish with increasing trophic level? 3) Do metal concentrations in water and fish present risks to human health in this ecosystem?

Materials and methods

Samples were collected in summer 2001 from three sites on Baiyangdian Lake (Duan Cun, Quan Tou, and Wangjia Zhai) that were at decreasing distances from wastewater discharge sources in Baoding City via the Fuhe River (closest to Wang Jia Zhai) and the Tanghe Sewage reservoir (Duan Cun, Figure 1). Quan Tou (low productivity, LP) was farthest from the sewage sources and considered to be the cleanest site. Duan Cun was located closest to the Tanghe Sewage Reservoir and had elevated nutrient levels (medium productivity, MP) and Wangjia Zhai was closest to the Fuhe River and industrial inputs from Baoding City resulting in the highest nutrient levels (high productivity site, HP). Most of the extent of the lake is comprised of shallow flooded areas and all of the sampling sites were between 3-4 meters. At each site we took samples for a variety of analyses: water chemistry (chlorophyll *a*, total N and total P, dissolved organic carbon (DOC)), and dissolved metal concentrations (total Hg and As). Environmental variables measured with a Hydrolab multiprobe included dissolved oxygen (DO), temperature, pH, and conductivity. Phytoplankton and zooplankton samples were collected as described in Chen et al. 2000. Phytoplankton taxonomy samples (<45 µm size) were collected and preserved in Lugol's solution. Phytoplankton biomass was calculated for each site by summing replicate sample abundance and biovolume data. Metal samples for particulates were filtered onto acid cleaned 0.4 µm Teflon filters and frozen. Samples for chlorophyll *a* samples were collected on Whatman GF/C filters, frozen, and sent out for analysis [Marker et al., 1980]. We collected micro- and macrozooplankton using 45 µm and 202 µm mesh plankton nets via vertical tows through the water column. Separate samples were collected for taxonomy, metal, and stable isotope (^{13}C) analyses. For taxonomy samples, zooplankton were anaesthetized in seltzer prior to preservation in buffered formalin [Stemberger and Lazorchak, 1994], and species were identified and enumerated under a dissecting scope. Metal concentrations were measured in filtered water (<0.4 µm), phytoplankton, zooplankton, and several fish species. Field blanks were collected and analyzed for all dissolved, phytoplankton, and zooplankton metal samples. ^{13}C was measured in zooplankton and fish.

All samples were collected from a non-metallic boat using trace metal clean technique and non-metallic sampling gear [Chen and Folt, 2005]. Prior to field sampling, Teflon storage containers for metal samples were acid cleaned in sequential concentrated HNO_3 , 2 M HCl and 0.33 M trace metal grade HNO_3 baths at 60°C. Field sampling for metal samples was conducted with great care to minimize contamination using previously established protocols [Patterson and Settle, 1976; Chen et al., 2000]. Dissolved metal samples were taken using a hand pump to draw water through acid cleaned LDPE tubing from a depth of 1 m and filtered through acid cleaned in-line 0.45 µm Gelman filters in the field. Procedural blanks for dissolved metal analysis were taken at each location. Dissolved metal samples were acidified in the field to pH 1 with Seastar Baseline HNO_3 (Seastar Chemical Inc., Sydney, BC, Canada) and analyzed directly without further digestion. Phytoplankton and zooplankton metal samples were digested in an aqua regia solution (2:1 Seastar Baseline HNO_3 and HCl, Seastar Chemical Inc., Sydney, BC, Canada) and heated to 70°C for 8-10 hours.

At each sampling location live fish were purchased from local fisherman who maintained their catch live in holding tanks within their boats. In the field, fish were handled using procedures to minimize contamination and were transported back to the lab in Beijing on ice. We kept all fish frozen throughout their transport back to the US until they were processed and analyzed at Dartmouth College. Each replicate fish was thawed and ground individually in a food processor with ultraclean water. Three 1.0 g samples from each fish were measured into separate Teflon vials. The food processor was cleaned thoroughly with Citranox (Alconox Inc.) and ultraclean water between fish samples. Prior to analysis, samples were digested in Seastar Baseline HNO_3 and peroxide and microwaved in a CEM MDS 2000 microwave.

All metal samples were analyzed in the Dartmouth Trace Element Analysis Core Facility using a magnetic sector inductively coupled plasma-mass spectrometer (ICP-MS ELEMENT, Finnigan MAT). Total Hg and As were analyzed using cold vapor/hydride generation ICP-MS [Klaue and Blum, 1999]. Detection limits ranged between 0.3-1.0 ng L^{-1} . All samples were quantified with matrix-matched NIST-traceable standard solutions (VHG, Manchester). External quality control was achieved by analyzing a standard reference material (NIST SRM 1640, Trace Element in water). Recovery rates ranged from 95-105% for Hg and As.

Samples for ^{13}C were collected in order to determine the carbon sources of the plankton and fish. The ratio of carbon isotopes (^{13}C) was used to evaluate the sources of carbon for an organism; high ^{13}C values identify littoral food sources from attached algae and detritus vs. low ^{13}C values which identify pelagic food sources from phytoplankton [France, 1995]. Stable isotope samples for fish were subsampled from homogenized fish tissue, freeze dried, and measured on a Carlo Erba CHN analyzer.

Metal concentrations in phytoplankton, zooplankton, and fish were compared between the three sampling sites (one-way ANOVA) and zooplankton data was log transformed and analyzed by site and size fraction using two-way ANOVA. Log K_d values for Hg and As were calculated based on measured dissolved metal concentrations and calculated phytoplankton dry weight calculations based on biovolume measurements. We used non-parametric Spearman Rank Correlation to test for possible associations between fish metal concentrations in individuals pooled across sites with fish body size, or ^{13}C . Correlations were analyzed for all species combined as well as for the single piscivorous species, *Channa argus*. All statistical analyses were performed with JMP (JMP version 5.01, SAS Institute, Inc., Cary NC).

Results

Water quality and phytoplankton density

Nutrient concentrations (total N and P, Table 1) increased progressively across the sites from Quan Tou (LP), the site farthest from nutrient inputs to Wangjia Zhai (HP) the site closest to sewage inputs. Significant differences in chlorophyll concentrations between the three sites followed the same spatial pattern (one-way ANOVA; $F=137.6$, $\text{d.f.}=2$, $p<0.0001$, Figure 2) with more phytoplankton at sites with greater nutrients (Figure 2). In contrast,

zooplankton abundance decreased with increasing phytoplankton biomass, thus total zooplankton density (45-202 μm size fraction) was lowest in the high productivity site, Wangjia Zhai (HP). However, statistical comparison of zooplankton dry weight biomass showed no significant differences between sites (Table 1, $F=1.54$, $d.f.=2$, $p=0.2473$). The pH profiles varied across sites with the highest pH at the lowest productivity site (Quan Tou, LP, 7.2-8.3), and the lowest pH at the highest productivity site (Wang Ji Zhai, HP, 6.2-7.4). In contrast to nutrient concentrations, dissolved concentrations of total Hg and As were highest at the lowest productivity site (LP), Quan Tou, and lowest at Wangjia Zhai, (HP) the highest productivity site (Figure 3). However, there were no significant differences between particulate concentrations (ng of metal/ mm^3 of cellular biovolume) of either metal across sites (Hg $p=0.1746$, As $p=0.2729$; Table 1). Log K_d values for Hg (5.11-6.10) and As (4.35-4.77) for all three sites were within the range measured for other contaminated systems (see Table 1).

Metal bioaccumulation in plankton

Total Hg and As concentrations in zooplankton differed in their pattern of bioaccumulation and their subsequent trophic transfer. In a two-way ANOVA, there were no significant differences in Hg concentrations in zooplankton between sites ($p=0.2481$), between size fractions ($p=0.7793$), or the interaction of the two ($p=.2922$). As concentrations also did not vary by site ($p=0.4037$) nor was there a significant interaction of site vs. size fraction ($p=0.6207$). However, As in zooplankton varied significantly by size fraction ($p=0.0003$); smaller size fractions (45-202 μm) had consistently higher As concentrations than large size fractions ($>202 \mu\text{m}$, Figure 3b). A two-way ANOVA for log ^{13}C in zooplankton also resulted in a significant size fraction effect ($p<0.0001$) with no significant site effect or interaction of site and size fraction ($p=0.3866$ and $p=0.0632$). Larger zooplankton were less depleted in ^{13}C than smaller zooplankton suggesting that larger zooplankton had more littoral sources of food and small zooplankton more pelagic sources. When metal burdens in small and large zooplankton and fish are compared, As concentrations diminished with trophic level at each site by up to 5 times where as Hg concentrations did not consistently decrease or increase with trophic level (Figure 3a and b).

Metal bioaccumulation in fish

Total Hg and As concentrations in fish were analyzed in 13 and 39 fish, respectively. Fish species included planktivores, omnivores, piscivores, and bottom feeders (Table 2). Due to analytical difficulties, data for the Hg in 26 of the original 39 fish sampled were lost. Across the remaining 13 fish, Hg concentrations in fish did not differ between sites ($p=0.4346$) and when data for 13 fish were log transformed, there was no relationship to ^{13}C ($p=0.6717$, Table 4). When metal concentrations for a single species, *Channa argus* (Hei Yu, total of 7 individuals), were pooled across sites and compared to fish variables using Spearman Rank Correlation (Table 4), Hg concentrations increased significantly with body weight ($p=0.0025$) and decreased significantly with increasing ^{13}C ($p=0.0362$). Comparing data from all fish ($n=39$), body weight and ^{13}C of fish did not vary significantly between sites. However, concentrations of As in fish were significantly higher in the highest productivity site (HP, Wangjia Zhai) than the other two sites ($p=0.0536$), Welch ANOVA test, Figure 3b). When As concentrations in all 39 fish were pooled across sites, As concentration was

negatively correlated with ^{13}C ($p < 0.0006$, Table 3). In the 7 *Channa argus* pooled across sites, As concentrations were not related to body weight ($p = 0.1482$) or ^{13}C ($p = 0.4316$) as they were for Hg.

Discussion

The bioaccumulation of Hg and As across trophic levels in the food web of Baiyangdian Lake varies by metal, the degree of metal contamination at each site, and site-specific nutrient enrichment and algal density. Based on the 13 fish we sampled and analyzed, Hg concentrations in fish are above critical threshold levels [USEPA, 2000; 2001] considered to pose some risk to humans and wildlife. A greater sample set is recommended given the potential human health hazards associated with high dietary Hg. Based on the larger sample of 39 fish for As, As concentrations are high enough to pose human health risks [Yoshida et al., 2004]. Since all the fish collected for the study were obtained from fisherman and destined for human consumption, these high metal burdens in Baiyangdian present a clear human health hazard.

Metal contaminants in Baiyangdian Lake come from a combination of point and non-point sources (agricultural runoff), and atmospheric deposition. Primary point sources are in the western sector of the lake in Baoding City where nutrient inputs from sewage and other contaminants from industrial sources are known to be great. Given its proximity to these sources, the Wangjia Zhai (HP) site was expected to have higher concentrations of contaminant in the water and biota. As observed in most lake studies, we found that nutrient enrichment resulted in high algal densities at this site [McQueen et al., 1992; Carpenter et al., 1998; Smith et al., 1999]. However, the dissolved concentrations of Hg and As were lowest there and highest in the most remote site, Quan Tou. Our own work and that of others has shown that nutrient enrichment and resulting algal blooms can be related to low dissolved concentrations of metal. It is suggested that algal biomass scavenges the metal from the dissolved fraction which also eventually deposits to the sediments as the bloom decays [Luoma et al., 1998; Chen et al., 2000]. High nutrients and algal densities are also related to lower Hg concentrations in zooplankton and fish suggesting a biodilution effect on trophic transfer [Kidd et al., 1999; Pickhardt et al., 2002; Kamman et al., 2004; Chen and Folt, 2005]. The chlorophyll concentrations Wangjia Zhai are as high as the highest levels in lakes in the Northeast US and total P concentrations are twice as high [Stemberger and Chen, 1998]. However, in this study, higher nutrient concentrations and algal densities did not result in higher zooplankton biomass, at least as measured on a single date suggesting that the high densities of blue green algal species were not highly edible and not transferred to secondary production. In contrast, lower algal biomass at Quan Tou was related to higher dissolved Hg concentrations and higher concentrations of Hg in small (45-202 μm) zooplankton fractions. When comparing the total metal concentrations in the dissolved and particulate fractions (ng/L) across sites, they were highest for both Hg and As in Quan Tou, the low nutrient site (Table 1). This suggests that the high algal biomass in the other two sites may result in major scavenging and storage of metals in the sediments which were not sampled in this study.

Total Hg bioaccumulation did not consistently increase with trophic level at the sites in Baiyangdian unlike patterns observed in previous studies of Hg, and particularly MeHg [Cabana et al., 1994; Watras et al., 1998; Chen et al., 2000; Power et al., 2002]. The lack of biomagnification of total Hg in the food web may be the result of high levels of eutrophication causing a biomass dilution of metal in the food web as seen in other productive lakes and in controlled experiments [Chen and Folt, 2000; Pickhardt et al., 2002; Chen and Folt, 2005]. However, given that the percent of total Hg as MeHg is known to increase with trophic level, MeHg may biomagnify in this food web as well (Chen and Folt unpublished data). Moreover, biomagnification of total Hg as observed across multiple lakes as seen in earlier studies may not be detectable in the limited amount of data from an individual lake [Cabana et al., 1994; Watras et al., 1998; Chen et al., 2000; Power et al., 2002].

The average Hg concentrations in fish were the highest at the lowest productivity site (Quan Tou, LP) of the three sites corresponding with the highest dissolved levels of Hg but differences between sites were not significant which may have been due to the limited sizes and species collected in each site. Within the single piscivorous species, *Channa argus*, collected across all 3 sites, there was a positive relationship between Hg concentration and body size and negative relationship of Hg to ^{13}C , patterns also observed in other studies [Lathrop et al., 1991; Driscoll et al., 1994; Lange et al., 1994]. Increasing Hg concentrations with size in freshwater fish has been attributed to 1) cumulative bioaccumulation of Hg over the lifetime of the fish resulting in higher concentrations in older fish and 2) ontogenetic shifts in diet with age such that older individuals consume prey with higher Hg concentrations [Driscoll et al., 1994]. The relationship of Hg to body size of *Channa argus* could be attributed to either of these mechanisms since the fish ranged from 137-398 g spanning a range of ontogenetic diet shifts. The negative relationship of Hg concentrations to ^{13}C suggests that larger fish with more Hg in their tissue have a more pelagic diet. Other studies also have shown fish with more pelagic diets (than benthic diets) have higher Hg concentrations in their tissue [Power et al., 2002; Gorski et al., 2003].

Arsenic concentrations in biota decreased with increasing trophic level demonstrating that As biodiminished in the food web. These results are consistent with previous studies that have also documented a biodiminution of As in aquatic food webs [Maeda, 1994; Chen and Folt, 2000]. This may be the result of relatively high levels of As excretion relative to assimilation in freshwater organisms [Maeda et al., 1992; Kuroiwa et al., 1994; Suhendrayatna et al., 2002]. Arsenic concentrations in zooplankton and in fish across sites also decreased with increasing ^{13}C suggesting that more pelagic pathways of carbon resulted in higher As bioaccumulation in biota [France, 1995]. In Baiyangdian, As concentrations were even higher in all compartments than in Upper Mystic Lake MA, a highly contaminated lake in the watershed of the Woburn Superfund site [Chen and Folt, 2000]. However, dissolved As concentrations in Baiyangdian were far lower than in the most contaminated basin of Spy Lake, MA USA associated with the Superfund site where dissolved metal concentrations were 100 $\mu\text{g/L}$ [Aurilio et al., 1995; Chen and Folt, 2000]. In both Baiyangdian and Upper Mystic Lake, concentrations of As were elevated in water and plankton but lower in fish.

Although China has some of the highest Hg emissions levels globally, relatively few studies have been conducted there on the bioaccumulation and biomagnification of Hg in freshwater fish, the main vector of Hg to humans [Li et al., 2006; Wu et al., 2006]. Total Hg concentrations measured in the environment and in biota comprise inorganic and organic species. MeHg, the organic species, is the form most readily assimilated and biomagnified in aquatic food webs and also the most toxic. Hg in fish is comprised almost entirely of MeHg (>95%) in top trophic level species, and thus, measured total Hg concentrations in fish such as *Channa argus*, a predatory species, very closely approximate MeHg concentrations.

Comparison of metal concentrations in Baiyangdian (0.01-0.33 mg total Hg/kg WW in whole body tissue) to the concentrations in 20 relatively uncontaminated lakes in the Northeast US shows Hg levels in water and biota to be within the range observed for the Northeast US region (Table 2) [Chen et al., 2000]. However, in terms of risk to fish consumers, the Baiyangdian fish Hg concentrations do exceed screening values for determining risk to avian, mammal, and human consumers of fish (0.05, 0.1, and 0.3 ppm MeHg per wet weight of fish, respectively) [USEPA, 2000; 2001]. Moreover, 0.3 ppm concentrations in fish filets most often consumed by humans are equivalent to whole body tissue concentrations of 0.185 ppm showing that the Baiyangdian whole body concentrations far exceed the human health criterion [Peterson et al., 2007]. The fish collected in this study were obtained from local fisherman who catch and sell their fish for human consumption in the region. According to USEPA, values in excess of their screening values should prompt action to conduct more extensive evaluation of human health risks [USEPA, 2000].

Relative to uncontaminated and contaminated lakes in the Northeast US, As concentrations in water and fish are greatly elevated in Baiyangdian and found at concentrations thought to cause risks to human health. Arsenic is a human carcinogen (i.e., lung, skin, bladder, and liver; [Wickre et al., 2004; Yoshida et al., 2004] and populations in China have been shown to be exposed via drinking water and food consumption [Pi et al., 2002; Liu et al., 2003]. Toxic forms of arsenic include inorganic species (As^{3+} and As^{5+}) as well as monomethylarsenite whereas arsenobetaines which are prevalent in seafood are considered benign [Shaw et al., 2007]. Arsenism is prevalent in areas where levels in water range from 0.05-2.0 mg/L still considerably higher than dissolved concentrations in Baiyangdian [Liu et al., 2003; Xia and Liu, 2004]. A human-health criterion exists in the US for total dissolved arsenic of 18 ng/L (estimated based on water and organism consumption; see below) or 140 ng/l (estimated based only on organism consumption) [USEPA, 1984]. This is a water column concentration thought to produce tissue burdens in fish that based on average human consumption would lead to cancer in 1 out of every million individuals. Dissolved metal concentrations in Baiyangdian are more than an order of magnitude higher than the criterion (140 ng/L vs. 8,194 ng/L) for human consumption of fish but considerably lower than contaminated wells in China [Liu et al., 2003; Xia and Liu, 2004]. Moreover, dissolved As concentrations in Baiyangdian are almost 8 times higher than concentrations in Upper Mystic Lake, MA USA [Aurillo et al., 1994; Aurilio et al., 1995; Neff, 1997; Chen and Folt, 2000; Kamman and Engstrom, 2002], a site known to have high levels of As from the nearby Woburn Superfund site. The As concentrations in fish are also up to 4 times higher in

Baiyangdian than Upper Mystic Lake and well above the range of As concentrations measured in lakes in the Northeast US [Chen and Folt, 2000; Chen et al., 2000].

Conclusion

The interaction of metal contamination and eutrophication in the industrialized Baiyangdian Lake in northeastern China appears to result in lower dissolved and particulate concentrations of both Hg and As in the presence of high algal densities. This may be due to scavenging of metals by algal biomass to sediments. Across sites, concentrations of Hg and As in fish were above values considered to pose risk to humans and wildlife based on USEPA criteria. However, the Hg concentrations in water and biota in the lake were not greater than concentrations in lakes in the northeast US despite the generally high levels of local Hg emission and deposition in China. High nutrients and algal density may be mitigating against even greater bioaccumulation. In contrast, As levels are very high and greater than those in the Northeast US, probably due to a contamination source in the watershed of the lake. Our results suggest that both Hg and As contamination should be investigated further due to the potential health risks to humans from drinking lake water or consuming fish.

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Figure 1. Map of Baiyangdian Lake in North China Plain with sample sites: 1) Duan Cun 2) Quan Tou, and 3) Wangjia Zhai.

Figure 2a

Figure 2b

Figure 2.

Relationships of chlorophyll *a* and dissolved metal concentrations to total phosphorus concentrations (TP): a) chlorophyll *a* concentration and phytoplankton biovolume vs. TP (Phytoplankton biovolume based on single taxonomy samples and chlorophyll values based on the mean $\pm$ SE of 3 replicates); b) dissolved metal concentrations (total Hg and As) to total phosphorus concentrations (dissolved metal concentrations based on one sample per site).

Figure 3a

Figure 3b

Figure 3.

Metal concentrations in biota at each site. Means + SE; a) Hg concentrations; and b) As concentrations. Letters a and b denote concentrations that differ significantly between zooplankton size fractions; c and d denote significant differences in fish metal concentrations (zooplankton and fish data were analyzed separately and not compared to one another).

Table 1

Physical, chemical, and biological parameters measured at each site. Calculation of partitioning coefficient (K_d) values based on calculations of dry weight Hg concentrations and dissolved Hg concentrations. ()=SE.

Parameter	Duan Cun	Quan Tou	Wangjia Zhai
pH	6.2-8.0	7.2-8.3	6.2-7.4
DOC (mg/L)	10.1	4.7	5.1
Total N (mg/L)	1.93	1.13	2.14
Total P (µg/L)	320	45	380
Chlorophyll <i>a</i> (µg /L)	75.3 (4.8)	14.3 (1.9)	94.7 (3.4)
Phytoplankton Biovolume (µm ³ ×10 ⁶ /L)	4.2	1.7	6.2
Total Zooplankton Abundance (#/L)	12.3	117.4	4.7
>202 Zooplankton biomass (DW mg)	5.5 (1.2)	4.8 (1.1)	3.1 (0.4)
Dissolved Hg (ng/L)	1.1	22.1	8.7
Dissolved As (ng/L)	5350	8190	4920
Particulate Hg (ng/mm ³ cell volume) ^a (ng/L of water) ^b	1.34 (0.41) ^a 5.63 ^b	2.85 (1.08) ^a 4.85 ^b	1.11 (0.57) ^a 6.88 ^b
Hg Log K_d	6.10	5.11	5.11
Particulate As (ng/mm ³ cell volume) ^a (ng/L of water) ^b	150 (4) ^a 630 ^b	184 (73) ^a 312 ^b	290 (38) ^a 1798 ^b
As Log K_d	4.45	4.35	4.77
DO (mg/L, surface to bottom)	8.0-0.1	6.8-0.4	11.4-4.5

Comparison of metal concentrations in water, zooplankton, and fish in Baiyangdian sites to typical concentrations found in Northeastern US lakes [Chen and Folt, 2000]. ND=no detection, QT=Quan Tou, DC=Duan Cun, and WJZ=Wangjia Zhai. Values for samples with replication are means with (1 standard error). Concentrations in bold for each metal in each Baiyangdian site exceed range of concentrations in NIEHS lakes.

Table 2

	Hg	DC	QT	WJZ	As	DC	QT	WJZ
	NIEHS				NIEHS			
Dissolved (µg/L)	ND-0.017	0.001	0.022	0.009	ND-0.587	5.344	8.194	4.921
45-202 µm (µg/g DW)	0.026-29.4	0.56 (0.13)	1.30 (0.16)	0.49 (0.49)	0-13.4	6.66 (1.68)	4.48 (0.69)	4.49 (0.96)
>202 µm (µg/g DW)	0.028-4.38	0.96 (0.29)	0.72 (0.12)	0.47 (0.39)	0-3.94	1.97 (0.52)	2.06 (0.50)	1.84 (0.27)
Fish (mg/kg WW)	0.05-1.38	0.12 (0.13)	0.15 (0.11)	0.07 (0.01)	0.01-0.08	0.06 (0.01)	0.10 (0.02)	0.144 (0.03)

Table 3

Spearman Rank Correlations of fish metal concentrations to fish variables across sites. ‘All’ fish includes all species analyzed for Hg or As pooled across all sites (n=number of fish used in statistical analyses). For each metal, data from the single species, *Channa argus*, were also analyzed. Values in bold are significant at the $p < 0.05$ level.

Metal	Fish Variable	Species	n	p-value	Spearman Rho
Hg	Body weight	All	13	0.6286	0.1484
	¹³ C	All	13	0.7890	-0.0824
	Body weight	<i>C. argus</i>	7	0.0025	0.9286
As	¹³ C	<i>C. argus</i>	7	0.0362	-0.7857
	Body weight	All	39	0.3277	0.1578
	¹³ C	All	39	<0.0006	-0.5426
	Body weight	<i>C. argus</i>	7	0.1482	-0.6017
	¹³ C	<i>C. argus</i>	7	0.4316	0.3571

Table 4

Fish species and their functional feeding groups collected in Baiyangdian lake at each site. Sites in which sample fish were collected for each metal analysis (Hg or As) are listed for each species: All = all three sites, QT = Quan Tou, DC = Duan Cun, and WJZ = Wangjiajia Zhai.

Scientific Names	Chinese Names	Feeding Group	Sites/Hg	Sites/As
<i>Hemiculter leucisculus</i>	Can Tiao	Planktivores	none	DC
<i>Channa argus</i>	Hei Yu	Piscivores	All	All
<i>Pseudobagrus fulvidraco</i>	Huang Sang(Ga Yu)	Piscivores	QT	All
<i>Carassius auratus</i>	Ji Yu	Omnivores	DC	DC, WJZ
<i>Misgurnus anguillicaudatus</i>	Li Qiu	Saprophagous	none	DC
<i>Silurus asotus</i>	Nian Yu	Piscivores	DC, QT	DC, QT
<i>Rhodeus atremius</i>	Pang Pi Yu	Omnivores	none	DC
<i>Aplocheilichthys latipes</i>	Qing Jiang	Omnivores	none	DC
<i>Fluta alba</i>	Shan Yu(eel)	Piscivores (Carnivores)	none	QT
<i>Hypophthalmichthys molitrix</i>	Bai Lian Yu	Planktivores	WJZ	WJZ